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Removal of SO2 from Industrial Waste Gases

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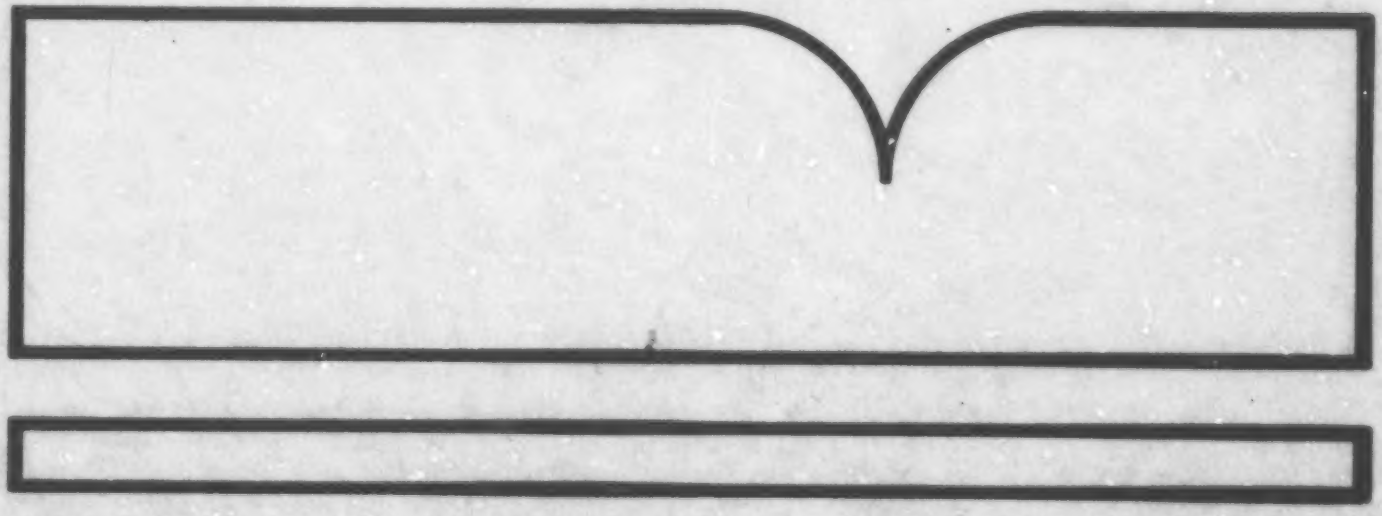

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16. ABSTRACT
The paper discusses technology for sulfur dioxide (SO2) pollution control by flue gas cleaning (called "scrubbing") in the utility industry, a technology that has advanced significantly during the past 5 years. Federal Regulations are resulting in increasingly large-scale applications for control of coal-fired boilers. With much less fanfare, control of SO2 in industrial process waste gases has been in use for some time in various industries. At first most applications were motivated by economic or aesthetic reasons; later, more by various pollution control regulations. Although the utility industry is responsible for most of the SO2 emissions, emissions from other industrial sources may have a greater effect, percentagewise, on ambient SO2 concentrations in populated areas. This is due mainly to height of the point of release of the waste gas (stack height), generally higher for utility systems (point sources) than for SO2 sources (area sources). With respect to combustion of sulfur-bearing fuels, accounting for more than 75% of the SO2 emissions, three basic control approaches can be taken: burn low-sulfur fuel, treat the fuel to reduce its sulfur content, and treat the waste gas to remove SO2. This paper concentrates on the third approach; treating waste gas to remove SO2.

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Sulfur Dioxide	Stationary Sources	07B
Flue Gases		21B
Scrubbers		07A, 13I
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Coal		21D
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Removal of SO_2 from industrial waste gases

Combustion of sulfur-bearing fuels accounts for more than 75% of SO_2 emissions in the U.S. These can be controlled to a degree by burning low-sulfur fuels or by pretreating the fuel to lower its sulfur content. Currently the most practical control involves scrubbing the gas to remove the sulfur dioxide.

Norman Kaplan and Michael A. Maxwell,
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☐ President Carter's plan to reduce this country's dependence on foreign oil stresses the conversion of oil- and gas-burning facilities to coal. This plan projects a massive need for scrubbers, since industrial coal converters will consume coal at a level of 60,000 MW equivalent by 1985. This compares with just 8,900 MW without the Carter plan [*1*].

WHY CONTROL SULFUR OXIDES?

Sulfur oxides have become among the more dangerous air pollutants to human health, and are clearly the most harmful to vegetation and to some building materials. Numerous epidemiological studies plainly show an association between air pollution, as measured by SO_2 concentration, and health effects of varying degrees of severity.

Mortality and morbidity can be correlated to ambient levels of SO_2, as evidenced during air-pollution episodes in New York City, Donora, Pa., and London, U.K. Adverse health effects do occur when 24-hour-average levels of SO_2 exceed 0.11 ppm for 3 to 4 days.

Sulfur dioxide is a highly toxic gas. For comparison, carbon monoxide, another gas with a reputation for high toxicity, causes adverse health effects only when concentrations exceed 9 ppm [*2*].

Synergism between SO_2 and Total Suspended Particulate matter (TSP) causes a combination of these pollutants to create more health problems than the sum of their individual effects would indicate. This has an obvious implication in the control of combustion sources that emit both SO_2 and particulate matter. In fact, today's primary air-quality standards for SO_2 and TSP were derived from population studies involving both pollutants [*3*].

More recent evaluations confirm that the two pollutants in association relate directly to health effects. However, their presence might only indicate the existence of other hazardous pollutants, such as sulfates. Evidence now shows that these other compounds may, in fact, be primarily responsible for the health effects originally attributed to SO_2 and TSP.

Atmospheric sulfates, especially sulfuric acid aerosol, are produced from SO_2 emissions through several chemical reactions in the atmosphere.

The presence of both SO_2 and TSP probably does indicate the presence of sulfates, although the converse does not necessarily hold true. It is possible to have high sulfate levels and low SO_2 or TSP, because sulfates may be windborne for considerable distances. For instance, sulfur dioxide emissions from rural sources (ore smelters or power plants out in the country) may be converted to sulfates and transported to areas where SO_2 emissions and atmospheric levels of SO_2 are low.

Development of a separate regulatory program for sulfates is an ultimate goal [*4*], but little information to

This article has been reviewed by the U.S. Environmental Protection Agency and approved for publication. Mention of tradenames or commercial products does not signify endorsement or recommendation for use.

Applicable regulations

As mandated by the 1970 Clean Air Amendments, the EPA administrator established six so-called "criteria pollutants" (particular matter, sulfur oxides, photochemical oxidants, carbon monoxide, hydrocarbons, and oxides of nitrogen) for which primary and secondary national ambient air-quality standards (NAAQS) were established. Primary standards were designed to protect public health, while secondary standards were prescribed to protect the public welfare:

NAAQS for sulfur oxides	Primary	Secondary
Annual mean	80 μg/m³ (0.03 ppm)	—
Maximum 24-h concentration*	365 μg/m³ (0.14 ppm)	—
3-h concentration*	—	1,300 μg/m³ (0.5 ppm)

*not to be exceeded more than once a year.

Summary of federal standards of performance limiting sulfur oxide emissions from new stationary sources **Table I**

Source category	Affected facilities	Maximum emissions
Fossil-fueled steam generators	Coal-fired boilers, oil-fired boilers (most utility and some industrial boilers)	Solid fuel: 2.2 g $SO_2/10^6$ cal (1.2 lb $SO_2/10^6$ Btu) Liquid fuel: 1.4 g $SO_2/10^6$ cal (0.80 lb $SO_2/10^6$ Btu)
Sulfuric acid plants	Process equipment	2 kg $SO_2/10^6$ cal (4 lb SO_2/ton of H_2SO_4) 0.075 kg acid mist/metric ton of H_2SO_4 (0.15 lb acid mist/ton H_2SO_4)
Petroleum refineries	Refinery process equipment, including waste-heat boilers and fuel-gas combustion devices	Fuel gas limited to 230 mg/dry Std. m^3 of H_2S (0.10 grains/dry Std. ft^3) maximum
Primary copper smelters	Roaster, smelting furnace, copper converter	0.065% SO_2 by volume
Primary zinc smelters	Roaster, sintering machine	0.065% SO_2 by volume
Primary lead smelters	Sintering machine, sintering-machine discharge end, dross reverberatory furnace, electric smelting furnace and converter	0.065% SO_2 by volume
Petroleum-refinery sulfur-recovery plants	Claus plants	0.025% SO_2 by volume (oxidation or reduction plus incineration) or 0.030% SO_2 by volume of reduced sulfur compounds, and 0.0010% by volume of H_2S (reduction only)

establish standards and control programs for sulfates now exists. A major research program is underway to find the sources and determine the transport of sulfates in the environment, to study chemical composition of sulfur compounds in the air, and to pin down specific health effects of these pollutants (see box). While research proceeds, regulatory programs to control SO_2 emissions appear to be the only practical means, however incomplete, of reducing levels of potentially hazardous sulfate aerosols in the air.

To meet the primary standards, the Clean Air Act amendments require each state to adopt (and submit to the Administrator) a State Implementation Plan (SIP) to provide for implementation, maintenance, and enforcement of the primary standard as soon as practicable, but not later than three years from the date of approval of the SIP. Requirements of SIP to implement, maintain and enforce the secondary standard must specify "a reasonable time at which such secondary standard will be attained."

New Source Performance Standard (NSPS) set by the Environmental Protection Agency with respect to sulfur oxides for a number of industrial source categories are provided in the Code of Federal Regulations (40 CFR, Part 60). Table I summarizes these NSPS, including also the NSPS for petroleum refinery, sulfur-recovery plants proposed by the *Federal Register* (41 Fr 43866) on October 4, 1976.

Between 1970 and 1975, more than 97% of sulfur oxide pollution in the U.S. resulted from fuel combustion in stationary burners and from industrial processes. The electric-utility industry caused about 60% of all SO_x pollution in that period; another 37% was split, half and half, between other stationary-source combustion and industrial processing; the remaining 3% resulted from miscellaneous sources, including combustion for transportation and solid waste.

About 60% of all the SO_x emissions from the industrial-process category (over 11% of the total) comes from metal refining and processing. Most of the remainder of this category comes from chemicals manufacturing, petroleum refining, and mineral-products processing. The chemical industry in 1975, as a case in point, accounted for 1.0 million tons of SO_x emissions,

or about 19.2% of the industrial-process output (which, in turn, was 15.8% of total U.S. discharge of SO_x that year).

UTILITY INDUSTRY SO_2 CONTROL

Well over 50 flue-gas-desulfurization (FGD) processes have been invented; many have undergone testing in small-scale laboratory or pilot-plant operations. But relatively few have served to date for SO_2 control of full-scale utility boilers in this country. In Japan, a few more systems have gone on to full operational status. For most purposes, a full-scale utility boiler is defined as one with a steaming rate equivalent to 100 MW of electric-generating capacity, with heat input of approximately 2.5×10^6 cal (10,000 Btu) per kWh generated.

In the United States, there are currently six types of FGD systems in use for controlling full-scale utility boilers. Table II summarizes these systems by type and extent of application. If alkaline-fly-ash scrubbing is considered a variation of lime-slurry scrubbing (since much of the alkalinity in the ash is due to CaO), the Table shows that 90% of all utility FGD operating capacity involves lime- or limestone-slurry scrubbing processes. These are "throwaway" processes, as opposed to "salable product" processes, since the SO_2 is removed in a form that must be discarded. Sodium carbonate scrubbing, also a throwaway process, has only limited application, since it produces a liquid waste-stream containing the sulfur in a soluble form (Na_2SO_4 and Na_2SO_3). (Nevada Power Co. uses this technology.)

The magnesium oxide and Wellman-Lord processes, on the other hand, produce salable sulfur products, such as elemental sulfur, sulfuric acid, or liquid sulfur dioxide (see Table II).

Utility flue-gas desulfurization processes* **Table II**

Process	No. of boilers	Total controlled generating capacity, MW
Lime-slurry scrubbing	9	2,702
Limestone-slurry scrubbing	6	2,037
Alkaline-fly-ash scrubbing	2	720
Sodium carbonate scrubbing	3	375
Magnesium oxide scrubbing	1	120
Wellman-Lord/ Allied Chemical	1	115
Total	22	6,069

*"Summary Report—Flue Gas Desulfurization Systems," Jan., Feb., Mar., 1977, PEDCo Environmental, Inc.

Lime/limestone-slurry scrubbing

In concept, lime- or limestone-slurry scrubbing processes are very simple. In practice, however, the chemistry and the system design for a full-scale operation can become more complex than seems evident at first glance.

These systems use a slurry of lime or limestone in water to absorb SO_2 from power-plant flue gas in a gas/liquid scrubber. The slurry generally ranges from 5% to 15% solids. Various types of scrubbers or gas/liquid contact devices are employed commercially: spray towers, venturis, marble-bed scrubbers (packed beds of glass spheres), and turbulent-contact absorbers (lightweight hollow plastic spheres—Ping Pong balls—held between restraining grids in a countercurrent scrubbing tower). These scrubbers usually operate with a liquid-to-gas (L/G) ratio of 6 to 15 L/normal m^3 (40 to 100 gal/1,000 actual ft^3).

Fig. 1, a schematic of the 10-MW prototype limestone system at the TVA/EPA test facility at TVA's Shawnee steam plant, shows a turbulent-contact absorber with an open chevron-type mist eliminator. Flue gas flows up through the tower and contacts slurry which sprays downward over the packing, countercurrent to the gas stream. The gas/liquid counterflow keeps the spheres in turbulent motion, which improves gas/liquid contact.

The overall absorption reaction taking place in the scrubber and the hold-tanks for a limestone-slurry system produces hydrated calcium sulfite:

$$CaCO_3 + SO_2 + \tfrac{1}{2}H_2O \rightarrow CaSO_3 \cdot \tfrac{1}{2}H_2O + CO_2 \quad (1)$$

With a lime-slurry system, the overall reaction is similar but yields no CO_2:

$$CaO + SO_2 + \tfrac{1}{2}H_2O \rightarrow CaSO_3 \cdot \tfrac{1}{2}H_2O \quad (2)$$

(The actual reactant in Eq. 2 is $Ca(OH)_2$, since CaO is slaked in the slurrying process.)

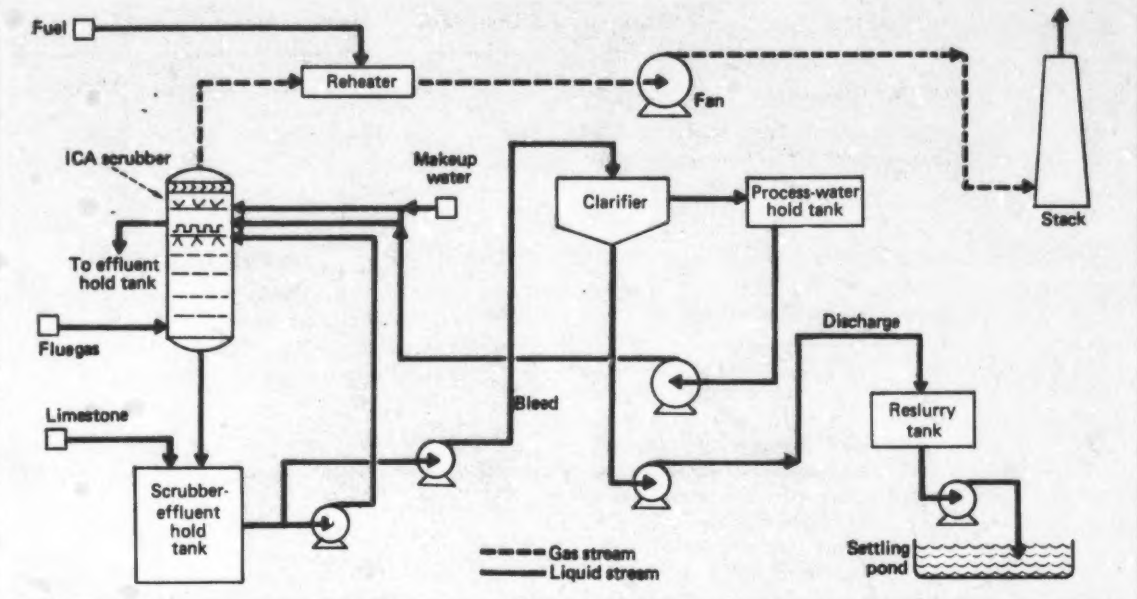
In practice, some of the absorbed SO_2 is oxidized by oxygen which is also absorbed from the flue gas. This shows up in the slurry as either gypsum ($CaSO_4 \cdot 2H_2O$) or as a calcium sulfite/sulfate mixed crystal [$Ca(SO_3)_x(SO_4)_y \cdot zH_2O$]. Slurry is recycled around the scrubber to obtain the high liquid-to-gas ratios required.

Lime- and limestone-slurry scrubbing systems can be engineered for almost any desired level of SO_2 removal. Commercial utility systems are generally designed for 80% to 95% removal; however, some systems have at times achieved more than 99% removal. The higher removal rate is not costly: investment savings realized in designing for 80% rather than 90% SO_2 removal amount to only about 3.2% to 4.5% [5].

Alkaline-fly-ash scrubbing

Western-U.S. low-sulfur coals appear particularly suitable to SO_2 control by scrubbing the waste gases with a slurry of the alkaline fly ash which results from the combustion process. There are two ways to add the alkaline ash to the system: (1) collecting the fly ash in an electrostatic precipitator upstream of the scrubber and then slurrying the dry fly ash with water so that it can be pumped into the scrubber circuit, and (2) scrubbing the fly ash directly from the flue gas by the circulating slurry of fly ash and water.

Most Western coals have a low sulfur content (less than 1.0%). They also usually have a low heating value and consequently require close control to hold their



Wet-limestone scrubbing system **Fig. 1**

combustion emissions within federal limits for New Source Performance Standards (NSPS), defined as mass emissions per unit heat input. While typical Eastern bituminous coals have heating values of about 22,000 cal/g (12,000 Btu/lb), lignite coals may have heating values as low as 12,000 cal/g (6,800 Btu/lb). The bituminous coal could contain as much as 0.7% sulfur and still meet the NSPS limitation of 2.2 g/10^6 cal, without controls. But the lignite would have to have no more than about 0.4% sulfur.

Generally, the coals best suited to this method of control are the Western lignites and sub-bituminous coals. Certain of these (from North Dakota, Montana, Wyoming) have large amounts of alkaline metal oxides in the ash (e.g., CaO, MgO).

Sodium carbonate scrubbing

This method of controlling SO_2 involves scrubbing the flue gas with a solution of sodium carbonate and bicarbonate, to produce a mixture of sodium sulfite and sulfate by these reactions:

$$Na_2CO_3 + SO_2 \rightarrow Na_2SO_3 + CO_2 \quad (3)$$

$$2\ NaHCO_3 + SO_2 + H_2O \rightarrow Na_2SO_3 + 2\ H_2O + 2\ CO_2 \quad (4)$$

$$Na_2SO_3 + \tfrac{1}{2}O_2 \rightarrow Na_2SO_4 \quad (5)$$

The sodium carbonate does not have to be pure. Nevada Power uses trona salt, a naturally occurring mineral containing 60% $NaHCO_3$, 20% NaCl, 10% sulfates, and 10% insolubles [6].

This process has definite limitations in large-scale utility applications, since it requires a relatively cheap source of sodium carbonate or bicarbonate and an ability to dispose of large volumes of waste salt solution. Nevada Power is located near trona deposits—in an area where natural evaporation rates far exceed rainfall and where available land is relatively abundant. The company processes its liquid waste in solar evaporation ponds and deposits the crystallized waste salts back at the mine.

Magnesium oxide scrubbing

The magnesium oxide process differs from any of the previously described processes in that it is a "regenerable" or "salable product" process rather than a "throwaway" operation. In other words, it does not produce waste material—SO_2 removed from the flue gas is concentrated and used to make marketable H_2SO_4 or elemental sulfur.

Employing a slurry of MgO—or $Mg(OH)_2$—to absorb SO_2 from flue gas in a scrubber, this process yields magnesium sulfite and sulfate. When dried and calcined, the mixed sulfite/sulfate produces a concentrated stream (10% to 15%) of SO_2 and regenerates MgO for recycle to the scrubber. Carbon added to the calcining step reduces any $MgSO_4$ to MgO and SO_2.

In commercial applications, the scrubbing and drying steps would normally take place at the power plant. The regeneration, and the sulfur or H_2SO_4 production steps, might be performed at a conventional sulfuric acid plant. Alternatively, a central processing plant could produce sulfur from mixed magnesium sulfite/sulfate brought in from other desulfurization locations.

Wellman-Lord system

The Wellman-Lord process (sold by Davy Powergas, Inc.) is also a regenerable, or salable-product, system.

When coupled with other processing steps, it can make salable liquid SO_2, H_2SO_4, or elemental sulfur.

The W-L process employs a solution of Na_2SO_3 to absorb SO_2 from waste gases in a scrubber or absorber, converting the sulfite to bisulfite:

$$Na_2SO_3 + SO_2 + H_2O \rightleftharpoons 2\ NaHSO_3 \quad (6)$$

Thermal decomposition of the bisulfite in an evaporative crystallizer can regenerate sodium sulfite for reuse as the absorbent:

$$2\ NaHSO_3 \xrightarrow{\Delta} Na_2SO_3 + SO_2 + H_2O \quad (7)$$

The evaporative crystallizer produces a mixture of steam and SO_2 and a slurry containing sodium sulfite/sulfate plus some undecomposed $NaHSO_3$ in solution. As water condenses from the steam/SO_2 mixture, it leaves a wet SO_2-enriched gas stream to undergo further processing for recovery of salable sulfur values.

NON-UTILITY STATIONARY-SOURCE COMBUSTION

Non-utility stationary-source combustion includes residential, commercial, and industrial heaters as well as industrial boilers to make steam for processing needs and, in some cases, to generate electricity for internal plant use [*7*].

It is difficult to classify emission sources on a common basis according to flue-gas flowrate, because at least six factors appear to influence these rates: (1) stoichiometric firing rate, (2) excess air, (3) leakage, (4) corrections for stack temperature, (5) boiler-load factor, and (6) fan-flow safety margin [*8*]. As a comparison, every megawatt of electric-generation capacity requires treatment of about 3,750 normal m^3/h (2,200 Std. ft^3).

Most of the flue-gas-desulfurization systems applicable to utility boilers can also control non-utility combustion sources. However, some important differences exist in these applications. For one thing, utility boilers generally release flue gas at about 150°C, while other combustion sources may discharge flue gas in the 200 to 260°C range. This higher-temperature flue gas can serve more effectively for stack-gas reheat.

It also generally holds true that non-utility combustion applications operate with higher excess-air rates than utilities do. As a result, the SO_2 will be more dilute and the oxygen more concentrated in the flue gas. This affects those wet-scrubbing systems, such as dual-alkali and Wellman-Lord, which respond adversely to high oxidation rates (i.e., oxidation of the sulfur species collected in solution: sulfites to sulfates).

Control equipment for non-utility systems, smaller than utility systems, lends itself better to shop fabrication than to field erection. For small-size applications, "package" or skid-mounted systems are available.

Frequently, industrial users of FGD systems will have excellent outlets, or uses, for the sulfur compounds they remove. For example, the pulp-and-paper industry can regenerate sodium sulfite scrubbing solutions in its manufacturing operation. The chemical industry often has captive markets for sulfuric acid. The petroleum industry has sources of H_2S that it can use to make sulfur from the SO_2 recovered in a regenerable FGD system.

Preliminary results of a continuing survey of SO_2-control systems for non-utility combustion and process sources [*9*] lists 27 known industrial-boiler FGD applications in the U.S., including 17 operational systems (Table III). More recent estimates indicate that the actual number and capacity of systems described in this survey may actually amount to two or three times these figures.

Sodium-alkali scrubbing

Most industrial boilers use a sodium-alkali scrubbing process—basically as described for sodium carbonate scrubbing in the utility-boiler section, and using sodium carbonate, bicarbonate, or hydroxide—which converts sulfur in the flue gas to sulfite/bisulfite and sulfate (Fig. 2).

Disposal practices for spent sodium-scrubbing liquors include: Consume in pulp/paper manufacturing; discharge to evaporation ponds; treat (mainly by air-oxidation) and discharge to city sewer system; and treat and discharge to rivers.

Many sodium-alkali users want to regenerate scrubber liquor by treating the spent liquor with calcium hydroxide. This would actually give them dual-alkali systems with the attendant advantage of eliminating a liquid-waste stream.

Dual alkali

Table III shows that dual-alkali systems have become the second most-prevalent type for SO_2 control of industrial boilers. They may become the first choice as more sodium alkali systems are converted to dual-alkali in the face of new regulations that may limit disposal of liquid wastes containing large amounts of dissolved salts (Fig. 2).

Dual-alkali processes, like lime/limestone-slurry scrubbing, are throwaway systems. In the operation as a whole, lime is consumed to produce a wet solid waste (mainly calcium sulfite/sulfate) just as in lime-slurry

The Ralph M. Parsons Co.

Twin-designed H_2SO_4 plant uses double catalysis/double absorption process Fig. 2

U. S. industrial-boiler SO_2-control systems **Table III**

Control system	No. of systems	Total equivalent capacity, MW*	Status
Sodium alkali scrubbing	12	783	Operational
	2	173	Under construction
	1	20	Not operating
Dual alkali	4	110	Operational
	2	200	Under construction
	1	12	Planned
	1	10	Not operating
Lime/limestone scrubbing	1	20	Operational
Wellman-Lord	1	100	Planned
Water scrubbing	1	1	Not operating
Citrate process	1	50	Under construction
Total	27	1,479	

*1 MW ≈ 4,500 kg/h (10,000 lb/h) of steam production.

scrubbing. Also, dual-alkali systems require a small amount of sodium-alkali makeup.

A solution of sodium sulfite/bisulfite and sulfate in a scrubber will absorb SO_2 from the flue gas or other waste gas. Only the sulfite is active in absorbing SO_2, forming bisulfite as in the Wellman-Lord system:

$$\textit{Absorption:}\ SO_3^{=} + SO_2 + H_2O \rightarrow 2\ HSO_3^{-} \quad (8)$$

The bisulfite-rich liquor, treated with lime in a reaction tank, regenerates active alkali for recycle to the scrubber.

$$\textit{Regeneration:}\ 2\ HSO_3^{-} + Ca(OH)_2 \rightarrow SO_3^{=} + CaSO_3\downarrow + 2\ H_2O \quad (9)$$

$$SO_4^{=} + Ca(OH)_2 \rightarrow 2\ OH^{-} + CaSO_4\downarrow \quad (10)$$

The sulfate and sulfite precipitate as a hydrated mixed crystal, or as a gypsum phase ($CaSO_4 \cdot 2\ H_2O$) plus a hydrated mixed crystal, depending upon the concentration of dissolved species. Also, depending upon solution concentrations, the mixed crystal is predominantly calcium sulfite, with up to about 25% calcium sulfate coprecipitated. Sulfite/bisulfite oxidation by oxygen in the flue gas produces sulfate in the system.

Lime/limestone slurry

The only lime-scrubbing system listed in Table III is the A. B. Bahco system installed at Rickenbacker Air Force Base. It controls SO_2 and particulate emissions from seven industrial boilers, equivalent to about 3 MW each.

The Bahco system, developed in Sweden, is sold in the U.S. by Research Cottrell, Inc., through a licensing agreement. Of particular interest for industrial boiler-size applications, it is sold as a package unit—i.e., offered in several standard sizes up to about 50 MW equivalent, with most of the unit preengineered and constructed before installation. The Bahco system consists of a two-stage vertical scrubber with a cyclone-type mist eliminator. The two stages operate in series, using flue-gas flow to entrain or inspirate the scrubber slurry. Bahco systems can use either lime or limestone slurry.

The boiler system at Rickenbacker burns 3.6%-sulfur coal with about 160% excess air. The scrubber is preceded by a mechanical dust collector, which is about 70% efficient. Lime was used in the scrubber initially but now limestone serves effectively. Underflow waste solid from a thickener discharges into a five-acre (0.02 km^2) Hypalon-lined disposal pond located about 120 meters from the scrubber. Clear water from the pond returns to the process. The system started operation in February 1976 and generally achieves about 90% SO_2 removal.

Citrate process

The single application of the citrate process shown in Table III is a 50-MW-equivalent system being installed by St. Joe Minerals Corp. at its G. F. Weaton Power Station under a project cofunded by St. Joe, U.S. Bureau of Mines, and EPA. The station burns 2.5%-sulfur coal and supplies power for St. Joe's zinc-smelting operation, and also sells power to the local grid. The process, being installed by United Engineers and Morrison-Knudsen, is designed to obtain 90% SO_2 removal. It should start operation in September 1978.

SO_2 is absorbed by a solution containing sodium sulfite, bisulfite, sulfate, thiosulfate, and polythionate. Citrate ion is present as a pH buffer, tying up hydrogen ions as un-ionized citric acid. The spent solution reacts with H_2S to precipitate elemental sulfur. The sulfur is concentrated by oil flotation or froth flotation, and the concentrated sulfur slurry then passes into a melter where the molten sulfur is drawn off. Approximately two thirds of the sulfur is used to produce H_2S by reaction with methane or water gas ($CO + H_2$), for recycle to the process. Regenerated solution must be processed to remove sulfates formed by oxidation in the absorbent loop. The sodium sulfate purge is reported to be 1 to 2% of the recovered sulfur [*10,11*].

METAL SMELTING

The metal-smelting processes—mainly copper, lead, and zinc—are second only to combustion processes in emissions of SO_2 in the U.S. Copper, lead, and zinc occur naturally as sulfides. To produce the metal, the sulfide ores are concentrated and then roasted or sintered to convert them to the metal oxides, with liberation of SO_2. The impure metal is then recovered by reduction of the oxides in electric reverbatory furnaces and flash-smelting systems.

Copper sulfide concentrates are normally roasted in either multiple-hearth or fluidized-bed roasters to remove the sulfur. About half of the smelters eliminate the roasting step and remove the sulfur as SO_2 by blowing the ore with air during the smelting operation. Lead sulfide, converted to the oxide in a sintering machine, is then reduced to the metal in a blast furnace. Fluidized-bed or multiple-hearth roasting, occasionally followed by sintering, removes sulfur from zinc ores. Metallic zinc is produced from the roasted ore by the horizontal or vertical retort process, or by the electrolytic process for high-purity zinc.

In the U.S., only two processes are used to control SO_2 emissions from copper, lead, and zinc smelters: (1) manufacture of byproduct sulfuric acid in single- and double-absorption systems, and (2) DMA N,N-dimethylaniline) process is the other (used at only two locations in the U.S.). In Japan, wet-limestone scrubbing and magnesium oxide scrubbing are also used. In British Columbia, the Canadians have used ammonium bisulfate scrubbing.

Smelter gases are classified as "weak" or "strong" SO_2 gases if SO_2 concentration runs, respectively, below or above 3.5 to 4%. These gases generally range in temperature from 600 to 1,000°C, considerably hotter than gases emitted from combustion of fossil fuels. As a first step in any processing for SO_2 removal, these gases must be conditioned by injecting water to cool and humidify them and to remove residual particulate matter. Storage and shipping considerations call for acid strengths of 93% and greater. Since the acid strength depends upon the SO_2 and moisture concentration of the processed gas, SO_2 concentration levels below 3.5 to 4% would require other, more expensive, means of gas cooling/drying (water balance) to produce concentrated sulfuric acid.

In addition, since the conversion of SO_2 to SO_3 is an exothermic reaction, sulfuric acid manufacture from smelter gases containing over 4% SO_2 is autogenous (requires no external heat). However, weak SO_2 streams do require heat to raise the temperature of the gases to the desired temperature (425 to 460°C) for catalytic conversion.

In the U.S., all of the strong (and none of the weak) SO_2 smelter gases are processed to control SO_2, although New Source Performance Standards (NSPS) will require control of both on any new plants. The preferred method of controlling SO_2 from new smelting plants is to design the plants initially to produce only strong SO_2 gas streams that can be controlled with byproduct sulfuric acid plants. Smelter-gas SO_2 concentration depends upon air leakage into the system and upon whether or not a large amount of fuel is burned with the amount of air required to sustain the roasting or smelting operation. Conversion of sulfides to oxides is exothermic, and so, with proper design, can be autogenous. In copper smelting, reverberatory furnaces that burn large amounts of fuel over the charge, produce gases containing 0.5 to 1.5% SO_2. The newer electric furnaces and flash-smelting systems, on the other hand, produce gases containing 4 to 6%, and 10 to 12%, SO_2 respectively.

Byproduct sulfuric acid manufacturing

The manufacture of sulfuric acid from smelter gas streams involves gas-conditioning, drying, catalytic conversion, and absorption [*12*].

Gas-conditioning may require a scrubbing tower, a cooler, and an electrostatic mist-precipitator, or other equivalent equipment combinations. To prevent acid contamination, minimize catalyst fouling, and reduce corrosion, this step removes particulate matter and cools the gas down to about 55°C.

The strong-SO_2 gases are dried in a tower using 93% sulfuric acid to absorb the moisture. In sulfuric acid plants, using weak-SO_2 gas feed, refrigeration may be necessary for part of the drying process.

Catalytic-converter feed-gases are preheated to 425 to 460°C by heat exchange with gases in the converter. The conversion reaction ($SO_2 + 1/2\,O_2 \rightarrow SO_3$) is exothermic. The gas stream then enters a three- or four-stage catalytic converter that uses a vanadium pentoxide catalyst to convert the SO_2 to SO_3. A staged reactor permits the reaction to take place at successively lower reaction temperatures, taking advantage of the trade-off between kinetics and equilibrium. High temperature increases reaction rate, but at the expense of conversion efficiency.

Gas leaving the final converter stage is cooled in a heat exchanger and fed to an absorber where concentrated sulfuric acid absorbs the SO_3. The gas stream leaving the absorber—containing small amounts of unabsorbed SO_3, unconverted SO_2, nitrogen, and oxygen—vents to the atmosphere.

In double-absorption (or double-contact, double-absorption) systems, the gas stream from the second or third stage of the reactor is cooled and passed through an absorber that uses concentrated acid to absorb SO_3. The gas, minus the absorbed SO_3, is then reheated to converter temperature and reintroduced into the third or fourth reactor stage. This double absorption allows a greater conversion of SO_2 to SO_3.

Typically, single-absorption sulfuric acid plants achieve an overall conversion efficiency of 98%, and the double-absorption plants can achieve in excess of 99.7% conversion (emissions of less than 250 ppm SO_2) [*13*]. Accordingly, the single-absorption plants generally do not meet NSPS, but the double-absorption plants do.

Dimethylaniline/xylidine process

In this process, the aromatic amines, DMA (N,N-dimethylaniline) or xylidine, absorb SO_2 from the gas stream. Xylidine is used in aqueous solution, DMA in an anhydrous form [*12*]. (U.S. systems use DMA as the absorbent.) The American Smelting and Refining Co. (ASARCO) developed the DMA/xylidine process in the late 1940s.

CHEMICAL INDUSTRY

Sulfuric acid plants

Sulfuric acid plants represent by far the major emitters of SO_2 in the chemical industry. All commercial sulfuric acid is made by either the lead-chamber process or the contact process. However, the contact process accounts for almost all of the acid produced in the U.S. and therefore is the only one considered here [*14*]. Categorized by raw material, 68% of the acid is produced in sulfur-burning plants; 18.5% by processing spent acid, refinery sludge, or hydrogen sulfide; and 13.5% by processing metal-smelter gases.

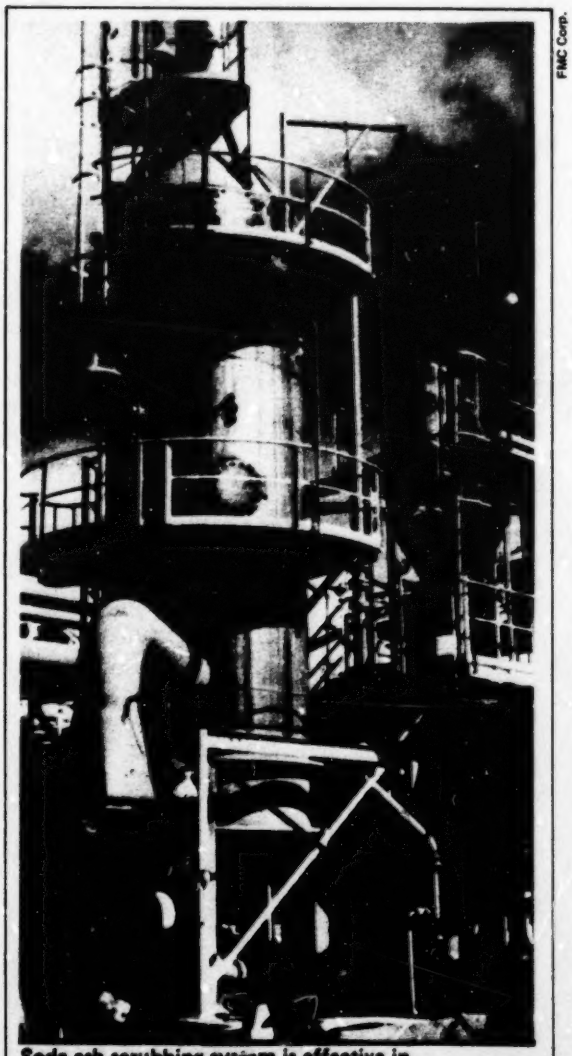
The identified control methods for U.S. sulfuric acid plants include double absorption, Wellman-Lord, and wet-limestone scrubbing, all of which were discussed previously [*9*]. The preferred method of SO_2 control with new, large contact sulfuric acid plants is the use of double-absorption (or double-contact, double absorption)—an integral part of the plant. Other SO_2 control

methods include ammonia scrubbing and molecular-sieve absorption.

Wood-pulp processes

Wood is processed to produce cellulose pulp for paper, wallboard, particle-board, and plywood by dissolving the lignin that binds the cellulose fibres together [*14*]. The principal processes used in chemical pulping are the kraft, sulfite, neutral sulfite semichemical (NSSC), and soda.

The kraft process uses an aqueous solution of sodium sulfide and sodium hydroxide in a pressurized digester, to dissolve the lignin from wood chips. This process accounts for about 60 to 65% of all the pulp produced in the U.S. The spent cooking liquor, called black liquor, is concentrated and burned in a recovery furnace to produce heat and dispose of the organic matter. By controlling the amount of excess air, Na_2CO_3 and Na_2S are collected in the bottom of the furnace as a molten smelt. This is reused after treatment with slaked lime to recausticize it. Calcium carbonate is calcined to lime for reuse.



FMC Corp.

Soda ash scrubbing system is effective in reducing high SO_2 concentrations **Fig. 3**

The kraft process emits a very characteristic odor, due to the presence of such sulfur compounds as H_2S, methyl mercaptan, and dimethyl sulfide. These compounds come from the various black-liquor concentration steps and from the recovery furnace. The various reduced-sulfur compounds can be incinerated to SO_2 (sometimes in the lime kiln) to cut down on the stronger odors that characterize reduced sulfur compounds.

Most of the remainder of the pulp is produced by the acid sulfite and NSSC processes, which emit mainly SO_2. The acid sulfite process uses a sulfurous-acid-based solution buffered with sodium, magnesium, calcium, or ammonium ion. The NSSC process uses sodium sulfite and bicarbonate solution. The SO_2 scrubbed from waste gases from these processes can be used as a makeup chemical for the system.

PETROLEUM REFINING, CLAUS PLANTS

Federal NSPS for SO_2 control in petroleum refineries, unlike other SO_2-control regulations, can limit the concentration of H_2S to about 160 ppm in the fuel gas burned, as a means of controlling SO_2 emissions, since most of the SO_2 emissions result from burning or incinerating gases containing hydrogen sulfide and other reduced-sulfur compounds. It is usually more economical in such cases to control SO_2 emissions by desulfurizing the fuel—treating it with an amine to absorb H_2S from the refinery gas. Subsequent regeneration of amine scrubbing liquid produces a concentrated H_2S stream, from which a Claus process can make elemental sulfur.

The Claus process, now a well-established technology, is primarily used to convert H_2S or mixtures of SO_2 and H_2S to elemental sulfur, as follows:

$$H_2S + 3/2\ O_2 \rightarrow SO_2 + H_2O \qquad (11)$$

$$SO_2 + 2H_2S \rightarrow 3S + 2H_2O \qquad (12)$$

$$\text{(overall)} \qquad 2H_2S + O_2 \rightarrow 2S + 2H_2O \qquad (13)$$

Claus plants can recover sulfur from sour natural gas, coke-oven gas, and other gases containing H_2S, in addition to refinery fuel gases.

In refineries, H_2S escapes from the barometric condensers on vacuum-distillation columns, from hydrocracking units, and from hydrogenation units. Regeneration of catalyst from catalytic-cracker units, combustion of spent acid sludges, and residues from various chemical treatment units produce the SO_2 emissions. Emissions of H_2S and SO_2 can be simultaneously treated in Claus plants to recover elemental sulfur, if the mole ratio of H_2S to SO_2 is greater than 2:1.

There are three principal approaches to tail-gas treatment in Claus systems [*15*]:

1. Continuation of the Claus reaction at lower temperatures on solid catalysts or in liquid media.
2. Catalytic hydrogenation of SO_2, COS, CS_2, and CH_3SH to H_2S, which is recovered by absorption.
3. Incineration of tail gas to convert all sulfur compounds to SO_2 followed by treatment through an SO_2-control system.

In the first category are the Sulfreen and the IFP-1500 processes. The Sulfreen process continues the Claus reaction in a fixed-bed reactor on a carbon or alumina catalyst at reduced temperature. The sulfur is retained on the catalyst and must be removed during regeneration by a hot inert gas. In the IFP-1500 process [*16*] the Claus reaction is extended at 120–130°C in a packed tower where Claus tail-gas contacts polyethylene glycol solvent containing a proprietary carboxylic acid catalyst. Sulfur is drawn off from the bottom of the tower as a liquid through a seal leg.

The Beavon and Shell SCOT (Shell Claus Offgas Treating) processes in the second category, are expected to make the largest impact in achieving the proposed NSPS for Claus plants. These processes use a cobalt molybdate catalyst to promote hydrolysis of CS_2 and COS, and provide hydrogenation of SO_2 to H_2S [*15*]. The SCOT process concentrates H_2S by absorbing it in an alkanolamine solution and then recycles it to the Claus plant. The Beavon process uses the Stretford process to oxidize the H_2S directly to elemental sulfur, while the SCOT process simply recycles the recovered H_2S to the Claus plant.

The third category of Claus tail-gas processes can use any acceptable SO_2-control process, after incineration of the tail gas, to convert all gaseous sulfur compounds to SO_2. These controls include those previously described, but certainly favor processes, such as Wellman-Lord, which produce a concentrated SO_2 stream. The SO_2 can then be recycled to the Claus plant to increase the yield of sulfur.

MINERALS PROCESSING

No Federal NSPS limits exist for SO_2 emissions from minerals-processing plants. However, some local regulations do require SO_2 control in certain areas.

Some of the industrial operations that emit sulfur oxides include: portland-cement kiln operations, fiberglass manufacturing, minerals- and chemicals-production from sulfate or sulfide ores, clay kilns, and production of expanded aggregate. In some mineral-process operations, sulfur in those minerals containing sulfates is reduced to SO_2 by a fossil fuel or coke that is burned in direct contact with the mineral. The fossil fuel itself also produces some of the SO_2 during combustion.

Some of the SO_2-control processes used in this type of operation include water scrubbing (with or without alkali addition for pH control, lime scrubbing, and dual-alkali scrubbing. In some cases, the mineral dust emitted from the process as particulate matter is itself alkaline and, when scrubbed from the process waste-gas in a wet scrubber, aids in control of SO_2.

An example of a mineral-process control system is the dual-alkali (or double-alkali) system installed at FMC's Modesto, Cal. (Fig. 3), chemical plant controlling emissions from two (barium and strontium) sulfate-reduction kilns [*17*]. The plant produces barium and strontium chemicals such as oxides, chlorides, carbonates, and nitrates by reducing the sulfates to oxides in the kilns, followed by further chemical processing. Charged with ore and coke, the kilns produce a high-temperature off-gas containing 4,000 to 8,000 ppm SO_2 at a maximum rate of about 26,000 normal m^3/h. This control system reportedly has achieved greater than 99% SO_2 removal, with greater than 95% operability since December 1971.

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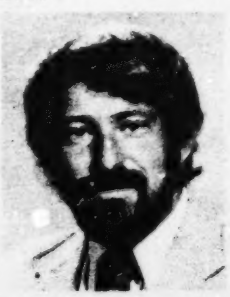

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